WATER-SOLUBLE OXIDANTS FOR CATALYSIS OF BUTADIENE-STYRENE COPOLYMERIZATION

BY

ORIN CLAWSON KEPLINGER, JR.

B.Ed., Southern Illinois State Teachers College, 1940
M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I am deeply grateful to my wife for her assistance — and persistance — throughout this work.

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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

The synthetic rubber interests of the United States became cognizant of "reductive-activation" or "redox" techniques of polymerization just after World War II (1-4). The increased activity of such catalysts has enabled present day workers to manufacture rubber at 0° to 5° at substantially the same rate as formerly obtained at 50°. The utility characteristics of such "cold rubber" are much to be preferred to those of the war-time GR-S (5). The current redox recipes have been developed with organic peroxides as oxidizing agents.

It has been felt in this laboratory that a definite effort should be made to develop fast recipes which use inorganic oxidizing agents. It became our object, then, to extend the field of redox catalysis to include a water soluble oxidant. It was further believed that an organic reducing agent would probably prove necessary.

Discussion Of Results

A variety of organic reducing agents have been used in attempts to develop a more successful redox couple with persulfates. The war-time "mutual" recipe (7) was modified by including benzoin, fructose, acetoin, or pyridine but without success.

An attempt was made to modify the carbonato tetrammine cobaltic nitrate recipe (8) so that the cobalt contamination of the product might be lowered. It was found that oxidizing agents such as air, ferric sulfate, and potassium ferricyanide were without effect. Potassium persulfate, or reducing agents such as ferrous sulfate or sorbose were detrimental. The pyrophosphate ion interfered with polymerization. No intermediate products which could be isolated during the prepara-

tion of the cobalt complex were found to be effective as catalysts.

Several runs were made using dodecyl sulfinic acid as a reducing agent in low p.H. emulsion polymerizations. The original German recipes of this type (9) were found to be ineffective without traces of air and iron. No equivalent substitute for the German emulsifier, Mersolat, has been found.

However, the search for an inorganic oxidant to catalyze polymerization has had a measure of success. The oxygen-mercaptan recipe which had been used for 50° polymerizations (10) but which did not function at 0° has been found capable of adjustment to promote conversions of 53% within thirty six hours at — 1°. This was made possible by incorporating traces of a cobalt salt in the recipe. A new emulsifier was required in the recipe since Rubber Reserve soap solidified at low temperatures. Potassium laurate has permitted more satisfactory polymerizations than have the potash soaps of hydrogenated tallow, oleic acid, or myristic acid, Nopco 2031, or Hercules Dresinate S-134. However, the purer potassium tetrahydroabietate which was derived from solutions of Dresinate S-134 by removing the settled neutral bodies also proved quite satisfactory. The recipe did not appear to require a soap aging procedure as had been the case with the 50° recipe. Baker's sodium pyrophosphate has again proved to serve well as a complexing agent for the iron. The optimum concentration of the reagent at 0° was about double the optimum level at 50°. A trace of iron in the form of ferrous sulfate was essential in the 0° recipe and served to couple the inorganic oxidant, oxygen, with the organic reducing agent, dodecyl mercaptan. Bottle pressure measurements which were taken throughout several of the polymerizations indicated a correspondence of one mole of oxygen to two moles of mercaptan and thus suggest initiation of polymerization by means of mercaptyl radicals. This was also indicated by the unusually high intrinsic viscosities — up to 4.36 — of rubber prepared by this recipe. The mercaptan could not have functioned to any great extent as a chain transfer agent. An excess of

oxygen, however, was avoided since it was found to inhibit polymerization completely.

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VITA

The author was born in Carlinville, Illinois on October 7, 1918. He attended public elementary schools in Detroit, Michigan and the Community High School in Carlinville, Illinois from which he was graduated in June, 1936. He attended Blackburn Junior College from September, 1936 until June, 1938 and Southern Illinois State Teachers College from September, 1938 until August 1940 when he received the degree of Bachelor of Education in zoology and chemistry. On August 20, 1940 he was employed as a chemical research assistant by the Western Cartridge Company of East Alton, Illinois. In September, 1941 he enrolled in night school classes in physical chemistry at Washington University which he completed in June, 1942. He participated in the development of continuous nitration processes for the manufacture of Tetryl and Nitroglycerine for which U.S. Patents 2,415,423 and 2,445,741 were granted. In June, 1944 he accepted a commission in the United States Navy where he served as an assistant gunnery officer aboard the destroyer, U.S.S. Cowie, and subsequently as an instructor in materials preservation at the naval base in San Diego, California. In May, 1946 he was returned to inactive duty and rejoined the research group at Western Cartridge Company as an assistant chemist. In September, 1946 he entered the Graduate School of the University of Illinois. He received the degree of Master of Science in June, 1948. Since September, 1946 he has held a special research assistantship on the Rubber Research Program.

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